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Role of Oxygen Vacancies in the Reduction of Nickel Oxide by Hydrogen

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Metal oxides are widely used as catalysts for the conversion of hydrocarbons in the chemical industry and the destruction of the sulfur dioxide and nitric oxide produced during the combustion of fuels in automobiles, factories and power plants. Though these catalysts have been designed empirically so far, scientists are now starting to understand how they operate. Using x-rays produced by the National Synchrotron Light Source, scientists from BNL and Yeshiva University in New York, have shown a direct oxidation of nickel oxide to nickel without accumulation of any intermediate phase, which may be explained by the presence of oxygen vacancies in the oxide. These results illustrate the complex role played by oxygen vacancies in the oxide reduction process.

Metal oxides are used as catalysts in a large variety of commercial processes for the conversion of hydrocarbons. Also, due to their low cost, metal oxides are also used as supports of many other catalytic materials. But in most cases, oxides alone are not very good catalysts. So, one method frequently used to prepare active oxide catalysts is to partially reduce the oxide with hydrogen at elevated temperature.

Reduction of nickel oxide by hydrogen has been the object of numerous studies, because nickel oxide is a component of many industrial catalysts and electromagnetic devices. So, we decided to look at the atomic mechanisms responsible for the reduction of nickel oxide under temperature ranging from 25 to 400 degrees Celsius. Such investigations resulted from the successful combination of very intense synchrotron radiation generated by the NSLS and new parallel data-collection devices installed at NSLS beamline X7B.

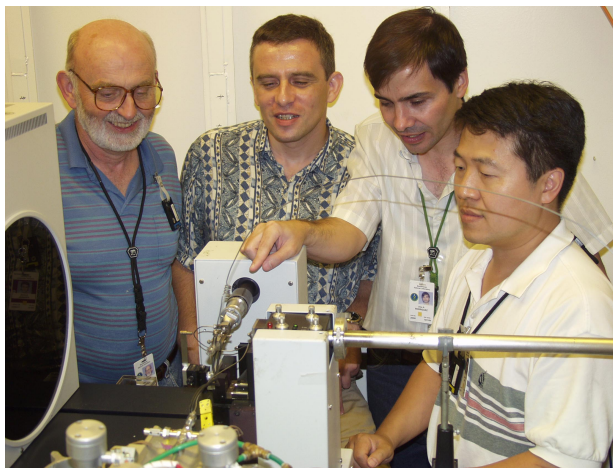
Experiments at beamline X7B have previously shown that *in situ* time-resolved x-ray diffraction (XRD) is a powerful technique to study oxide reduction. By using XRD and x-ray absorption techniques, we have shown that crystal and powder forms of nickel oxide are directly reduced to nickel at atmospheric pressures and elevated temperatures (250 to 350 degrees), but only after an induction – or delay – period.

During the induction period, oxygen vacancies are created within the crystal of nickel oxide. These

vacancies then favor the adsorption of hydrogen to the oxide and substantially lower the energy barrier associated with the cleavage of hydrogen bonds. At the same time, adsorbed hydrogen can induce the migration of oxygen vacancies from inside the nickel oxide crystal to the surface. By inducing more oxygen vacancies on the surface, the hydrogen atoms thus “autocatalyze” the oxide reduction process, which becomes more and more efficient over time.

XRD data collected by studying the reaction of hydrogen with a nickel oxide powder at 280 degrees Celsius are shown in **Figure 1**. During the first 50 minutes, the intensity of the diffraction lines for nickel oxide remains constant (red). Then, these lines begin to disappear while lines for metallic nickel appear (blue), but no line associated with a well-ordered intermediate phase is visible.

By using near-edge and extended x-ray absorption fine structure (NEXAFS/EXAFS) techniques at



Members of the team who conducted the study (from left to right): Jon Hanson, Anatoly Frenkel, Jose Rodriguez (lead author) and Jae Kim.

beamline X16C, we also observed a similar induction time. One might argue that an amorphous phase (NiO_x , $0 < x < 1$), with special chemical properties, might form during the induction time. This possibility was ruled out by the NEXAFS data shown in **Figure 2**, which reveal only two compounds after oxide reduction: the produced nickel and

the nickel oxide that was left from the reaction. (If an amorphous phase were created, the curve in **Figure 2** would have a different line shape, corresponding to three compounds: nickel, nickel oxide and the amorphous phase.)

Our studies indicate that oxygen vacancies play a key role in the

reduction of nickel oxide, by generating the necessary sites for the dissociation of molecular hydrogen and the subsequent auto-activation of the oxide catalyst.

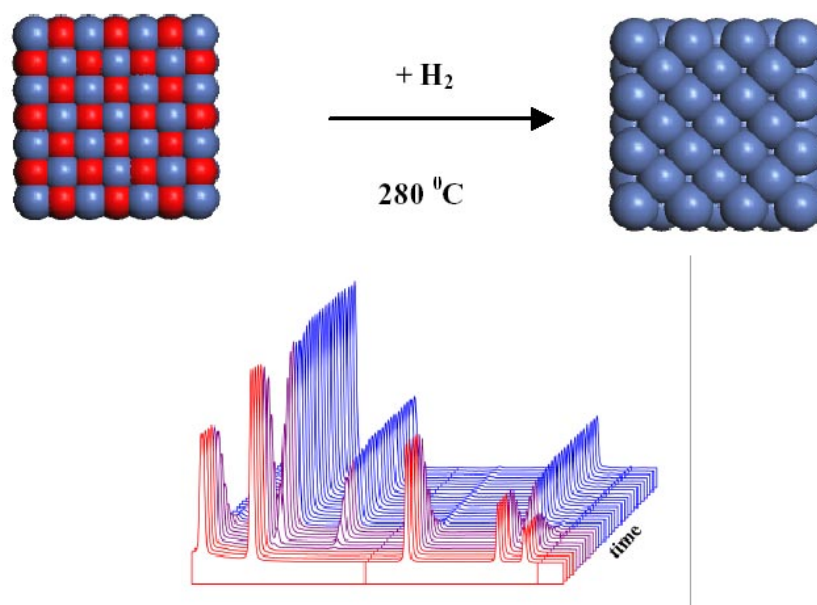


Figure 1. (Top) Crystal structure of nickel oxide and nickel (nickel: blue; oxygen: red). (Bottom) Time-resolved x-ray diffraction results for the reaction of a nickel oxide powder with hydrogen at 280 degrees Celsius (red lines: nickel oxide; blue lines: nickel).

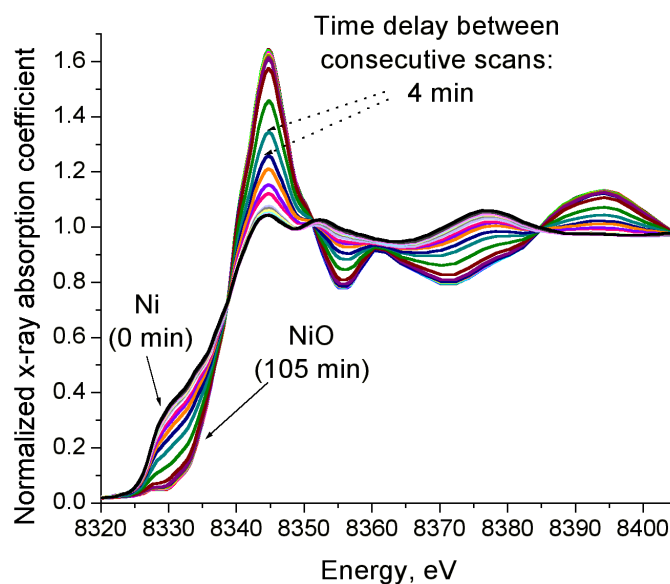


Figure 2. Time-resolved near-edge x-ray absorption fine structure (NEXAFS) data for the reduction of nickel oxide powder at 280 degrees Celsius under a flow of hydrogen.